Supporting Information

Spectroscopic and Computational Studies on $[(PhTt^{tBu})_2Ni_2(\mu\text{-}O)_2]$: Nature of the Bis-$\mu$-oxo $(Ni^{3+})_2$ "Diamond" Core

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Table S1. Atomic coordinates of an approximate model of $[(PhTt^{tBu})_2Ni_2(\mu\text{-}O)_2]$ **1** obtained from a symmetry-unrestricted DFT geometry optimization in the $S = 1, |M_S| = 1$ HS state, associated with two ferromagnetically coupled low-spin ($S = 1/2$) Ni^{3+} centers.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.378	0.006	0.003	H32	2.956	3.846	0.888
Ni2	-1.378	-0.006	0.003	H33	1.291	3.147	0.775
O3	0.026	1.210	-0.003	H34	2.430	2.563	2.042
O4	-0.026	-1.210	-0.003	H35	5.248	1.834	0.088
S5	2.598	-1.045	1.765	H36	4.487	1.254	1.592
S6	2.900	1.677	-0.169	H37	2.666	-1.214	-3.971
S7	2.626	-1.304	-1.550	H38	1.021	-0.955	-3.296
S8	-2.598	1.045	1.765	H39	2.223	0.382	-3.263
S9	-2.900	-1.677	-0.169	H40	4.959	-1.601	-1.923
S10	-2.626	1.304	-1.550	H41	4.497	0.103	-2.144
C11	1.783	-2.650	2.066	H42	7.019	0.028	-0.696
C12	4.269	-1.526	1.152	H43	6.978	-0.297	1.046
C13	2.342	2.946	1.018	H44	6.855	-1.637	-0.108
C14	4.517	1.117	0.498	H45	-2.350	3.194	2.832
C15	2.084	-0.704	-3.192	H46	-0.768	2.437	2.419
C16	4.389	-0.769	-1.478	H47	-1.732	3.223	1.133
C17	6.536	-0.595	0.078	H48	-4.897	1.602	2.055
C18	-1.783	2.650	2.066	H49	-4.175	2.537	0.723
C19	-4.269	1.526	1.152	H50	-2.956	-3.846	0.888
C20	-2.342	-2.946	1.018	H51	-1.291	-3.147	0.775
C21	-4.517	-1.117	0.498	H52	-2.430	-2.563	2.042
C22	-2.084	0.704	-3.192	H53	-5.248	-1.834	0.088
C23	-4.389	0.769	-1.478	H54	-4.487	-1.254	1.592
C24	-6.536	0.595	0.078	H55	-2.666	1.214	-3.971
B25	-4.907	0.444	0.063	H56	-1.021	0.955	-3.296
B26	4.907	-0.444	0.063	H57	-2.223	-0.382	-3.263
H27	2.350	-3.194	2.832	H58	-4.959	1.601	-1.923
H28	0.768	-2.437	2.419	H59	-4.497	-0.103	-2.144
H29	1.732	-3.223	1.133	H60	-7.019	-0.028	-0.696
H30	4.897	-1.602	2.055	H61	-6.978	0.297	1.046
H31	4.175	-2.537	0.723	H62	-6.855	1.637	-0.108

Table S2. Atomic coordinates of an approximate model of $[(PhTt^{tBu})_2Ni_2(\mu\text{-}O)_2]$ **1** obtained from a symmetry-unrestricted DFT geometry optimization in the $M_S = 0$ BS state, associated with two exchange-coupled low-spin ($S = 1/2$) Ni^{3+} centers.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.384	0.027	-0.003	H32	2.890	3.899	0.897
Ni2	-1.385	-0.027	0.010	H33	1.235	3.180	0.778
O3	0.000	1.203	-0.003	H34	2.380	2.604	2.043
O4	0.000	-1.203	-0.003	H35	5.212	1.939	0.078
S5	2.614	-0.998	1.740	H36	4.466	1.335	1.580
S6	2.865	1.736	-0.174	H37	2.667	-1.114	-3.986
S7	2.630	-1.238	-1.568	H38	1.016	-0.901	-3.308
S8	-2.568	0.973	1.803	H39	2.189	0.462	-3.255
S9	-2.878	-1.726	-0.161	H40	4.964	-1.494	-1.953
S10	-2.665	1.281	-1.489	H41	4.473	0.204	-2.163
C11	1.839	-2.624	2.042	H42	7.008	0.167	-0.729
C12	4.292	-1.445	1.123	H43	6.981	-0.169	1.012
C13	2.287	2.990	1.021	H44	6.876	-1.504	-0.148
C14	4.495	1.206	0.485	H45	-2.357	3.118	2.887
C15	2.074	-0.628	-3.201	H46	-0.759	2.389	2.475
C16	4.384	-0.673	-1.500	H47	-1.730	3.169	1.188
C17	6.539	-0.469	0.044	H48	-4.863	1.517	2.146
C18	-1.777	2.588	2.119	H49	-4.176	2.456	0.794
C19	-4.254	1.443	1.228	H50	-2.878	-3.920	0.851
C20	-2.271	-3.013	0.983	H51	-1.223	-3.195	0.711
C21	-4.484	-1.206	0.560	H52	-2.337	-2.653	2.019
C22	-2.135	0.748	-3.160	H53	-5.217	-1.930	0.165
C23	-4.414	0.703	-1.400	H54	-4.419	-1.352	1.653
C24	-6.541	0.483	0.216	H55	-2.749	1.263	-3.913
B25	4.908	-0.345	0.039	H56	-1.082	1.035	-3.273
B26	-4.908	0.355	0.152	H57	-2.244	-0.342	-3.261
H27	2.430	-3.157	2.797	H58	-5.008	1.526	-1.835
H28	0.824	-2.438	2.407	H59	-4.509	-0.169	-2.071
H29	1.792	-3.194	1.106	H60	-7.040	-0.145	-0.546
H30	4.922	-1.513	2.026	H61	-6.946	0.173	1.197
H31	4.217	-2.456	0.689	H62	-6.884	1.520	0.045

Table S3. Atomic coordinates of an approximate model of $[(\mathrm{PhTt}^{t\mathrm{Bu}})_2\mathrm{Ni}_2(\mu\text{-O})_2]$ **1** obtained from a symmetry-unrestricted DFT geometry optimization in the $S = 3, |M_S| = 3$ HS state, associated with two ferromagnetically coupled high-spin ($S = 3/2$) Ni^{3+} centers.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.328	-0.093	0.005	H32	2.933	4.038	0.889
Ni2	-1.328	0.093	0.005	H33	1.283	3.321	0.735
O3	0.005	1.358	-0.005	H34	2.391	2.752	2.028
O4	-0.005	-1.358	-0.005	H35	5.277	2.078	0.116
S5	2.662	-0.928	1.785	H36	4.507	1.454	1.593
S6	2.914	1.852	-0.172	H37	2.793	-1.063	-4.033
S7	2.728	-1.184	-1.619	H38	1.124	-0.928	-3.386
S8	-2.662	0.928	1.785	H39	2.230	0.491	-3.317
S9	-2.914	-1.852	-0.172	H40	5.067	-1.323	-1.957
S10	-2.728	1.184	-1.619	H41	4.503	0.356	-2.156
C11	1.964	-2.587	2.109	H42	7.052	0.303	-0.707
C12	4.340	-1.317	1.122	H43	7.012	-0.025	1.034
C13	2.329	3.128	0.998	H44	6.927	-1.368	-0.123
C14	4.548	1.344	0.496	H45	-2.579	3.087	2.868
C15	2.164	-0.603	-3.260	H46	-0.940	2.449	2.472
C16	4.445	-0.532	-1.506	H47	-1.943	3.166	1.178
C17	6.582	-0.335	0.064	H48	-4.978	1.382	2.019
C18	-1.964	2.587	2.109	H49	-4.274	2.328	0.685
C19	-4.340	1.317	1.122	H50	-2.933	-4.038	0.889
C20	-2.329	-3.128	0.998	H51	-1.283	-3.321	0.735
C21	-4.548	-1.344	0.496	H52	-2.391	-2.752	2.028
C22	-2.164	0.603	-3.260	H53	-5.277	-2.078	0.116
C23	-4.445	0.532	-1.506	H54	-4.507	-1.454	1.593
C24	-6.582	0.335	0.064	H55	-2.793	1.063	-4.033
B25	-4.950	0.202	0.049	H56	-1.124	0.928	-3.386
B26	4.950	-0.202	0.049	H57	-2.230	-0.491	-3.317
H27	2.579	-3.087	2.868	H58	-5.067	1.323	-1.957
H28	0.940	-2.449	2.472	H59	-4.503	-0.356	-2.156
H29	1.943	-3.166	1.178	H60	-7.052	-0.303	-0.707
H30	4.978	-1.382	2.019	H61	-7.012	0.025	1.034
H31	4.274	-2.328	0.685	H62	-6.927	1.368	-0.123

Table S4. Atomic coordinates of an approximate model of $[(\mathrm{PhTt}^{t\mathrm{Bu}})_2\mathrm{Ni}_2(\mu\text{-O})_2]$ **1** obtained from a DFT geometry optimization in the $S = 1, |M_S| = 1$ HS state in C_{2h} symmetry, associated with two ferromagnetically coupled low-spin ($S = 1/2$) Ni^{3+} centers.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.384	-0.002	0.000	H32	2.247	-3.120	2.954
Ni2	-1.384	0.002	0.000	H33	0.800	-2.609	1.999
O3	-0.012	-1.191	0.000	H34	2.199	-3.359	1.170
O4	0.012	1.191	0.000	H35	4.902	-0.986	2.260
S5	2.568	-1.028	1.787	H36	4.462	-2.428	1.326
S6	3.084	1.548	0.000	H37	2.199	-3.359	-1.170
S7	2.568	-1.028	-1.787	H38	0.800	-2.609	-1.999
S8	-2.568	1.028	1.787	H39	2.247	-3.120	-2.954
S9	-3.084	-1.548	0.000	H40	4.902	-0.986	-2.260
S10	-2.568	1.028	-1.787	H41	4.462	-2.428	-1.326
C11	2.939	3.375	0.000	H42	6.903	-1.576	0.883
C12	4.836	1.009	0.000	H43	6.903	-1.576	-0.883
C13	1.892	-2.711	2.000	H44	7.228	-0.082	0.000
C14	4.351	-1.332	1.370	H45	-2.413	-3.711	0.900
C15	1.892	-2.711	-1.000	H46	-2.413	-3.711	-0.900
C16	4.351	-1.332	-1.370	H47	-3.963	-3.768	0.000
C17	6.596	-0.988	0.000	H48	-5.309	-1.437	0.898
C18	-2.939	-3.375	0.000	H49	-5.309	-1.437	-0.898
C19	-4.836	-1.009	0.000	H50	-2.247	3.120	-2.954
C20	-1.892	2.711	-1.000	H51	-0.800	2.609	-1.999
C21	-4.351	1.332	-1.370	H52	-2.199	3.359	-1.170
C22	-1.892	2.711	2.000	H53	-4.902	0.986	-2.260
C23	-4.351	1.332	1.370	H54	-4.462	2.428	-1.326
C24	-6.596	0.988	0.000	H55	-2.247	3.120	2.954
B25	4.972	-0.642	0.000	H56	-0.800	2.609	1.999
B26	-4.972	0.642	0.000	H57	-2.199	3.359	1.170
H27	2.413	3.711	-0.900	H58	-4.902	0.986	2.260
H28	2.413	3.711	0.900	H59	-4.462	2.428	1.326
H29	3.963	3.768	0.000	H60	-6.903	1.576	0.883
H30	5.309	1.437	-0.898	H61	-7.228	0.082	0.000
H31	5.309	1.437	0.898	H62	-6.903	1.576	-0.883

Table S5. Atomic coordinates of an approximate model of $[(PhTt^{tBu})_2Ni_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]$ **2** as obtained from a DFT geometry optimization in the $M_S = 0$ BS state.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.821	0.211	0.111	H32	3.042	4.425	0.438
Ni2	-1.822	-0.210	0.110	H33	1.408	3.764	0.100
O3	0.000	0.746	-0.110	H34	2.221	3.384	1.655
O4	-0.000	-0.748	-0.110	H35	5.385	2.534	0.309
S5	2.767	-0.397	2.127	H36	4.456	2.125	1.772
S6	3.104	2.093	-0.220	H37	3.700	-1.464	-3.436
S7	3.300	-1.155	-1.068	H38	1.955	-1.280	-3.054
S8	-2.731	0.371	2.154	H39	3.018	0.168	-3.095
S9	-3.114	-2.085	-0.237	H40	5.684	-1.216	-1.065
S10	-3.336	1.177	-0.998	H41	5.082	0.353	-1.652
C11	2.139	-2.048	2.606	H42	7.387	0.804	0.067
C12	4.566	-0.698	1.842	H43	7.123	0.844	1.820
C13	2.372	3.568	0.584	H44	7.288	-0.712	0.983
C14	4.660	1.819	0.732	H45	-2.539	2.315	3.591
C15	2.964	-0.900	-2.849	H46	-0.995	1.916	2.755
C16	4.972	-0.401	-0.855	H47	-2.308	2.750	1.854
C17	6.854	0.301	0.895	H48	-4.994	0.530	2.883
C18	-2.083	2.013	2.638	H49	-4.629	1.765	1.653
C19	-4.529	0.693	1.895	H50	-3.027	-4.443	0.325
C20	-2.353	-3.589	0.481	H51	-1.405	-3.763	-0.046
C21	-4.629	-1.844	0.783	H52	-2.163	-3.448	1.554
C22	-3.034	1.007	-2.798	H53	-5.368	-2.561	0.383
C23	-5.001	0.404	-0.767	H54	-4.379	-2.157	1.813
C24	-6.839	-0.321	1.017	H55	-3.789	1.588	-3.345
B25	5.232	0.259	0.647	H56	-2.032	1.410	-3.002
B26	-5.225	-0.264	0.728	H57	-3.078	-0.051	-3.094
H27	2.608	-2.351	3.551	H58	-5.722	1.219	-0.951
H28	1.054	-1.963	2.735	H59	-5.121	-0.339	-1.575
H29	2.363	-2.777	1.816	H60	-7.387	-0.852	0.217
H30	5.045	-0.517	2.818	H61	-7.074	-0.842	1.964
H31	4.674	-1.771	1.611	H62	-7.285	0.689	1.091

Table S6. Atomic coordinates of an approximate model of $[(Tp^{Me_3})_2Ni_2(\mu\text{–}O)_2]$ **4** employed in single-point DFT computations.

atom	x/Å	y/Å	z/Å	atom	x/Å	y/Å	z/Å
Ni1	1.441	0.000	0.000	C29	-4.719	2.404	0.455
Ni2	-1.441	0.000	0.000	C30	-3.846	3.267	1.144
O3	0.019	1.168	0.001	C31	-2.646	2.592	1.218
O4	-0.019	-1.169	-0.001	C32	-2.768	-2.611	1.127
N5	2.238	-0.017	1.876	C33	-3.991	-3.173	1.173
N6	3.628	-0.004	1.985	C34	-4.847	-2.281	0.501
N7	2.766	1.413	-0.501	B35	4.435	-0.060	0.699
N8	4.094	1.213	-0.147	B36	-4.434	0.060	-0.699
N9	2.716	-1.426	-0.565	H37	0.652	-0.031	3.307
N10	4.024	-1.308	-0.098	H38	2.740	0.038	5.137
N11	-2.237	0.017	-1.876	H39	5.018	0.085	3.605
N12	-3.627	0.004	-1.985	H40	1.837	3.037	-1.528
N13	-4.093	-1.213	0.147	H41	4.315	4.127	-1.614
N14	-2.765	-1.414	0.501	H42	5.922	2.351	-0.277
N15	-2.715	1.426	0.565	H43	1.754	-2.956	-1.751
N16	-4.024	1.307	0.098	H44	4.064	-4.265	-1.553
C17	1.736	-0.004	3.119	H45	5.782	-2.527	-0.200
C18	2.840	0.032	4.041	H46	5.440	-0.096	0.912
C19	3.974	0.039	3.263	H47	-5.018	-0.065	-3.605
C20	2.768	2.610	-1.127	H48	-2.740	-0.038	-5.137
C21	3.991	3.173	-1.173	H49	-0.652	0.010	-3.307
C22	4.847	2.281	-0.501	H50	-5.440	0.096	-0.912
C23	2.646	-2.593	-1.218	H51	-5.787	2.518	0.218
C24	3.847	-3.267	-1.144	H52	-4.064	4.265	1.553
C25	4.719	-2.405	-0.455	H53	-1.749	2.964	1.734
C26	-3.973	-0.040	-3.263	H54	-1.840	-3.028	1.546
C27	-2.840	-0.032	-4.041	H55	-4.319	-4.118	1.632
C28	-1.735	0.004	-3.119	H56	-5.917	-2.361	0.258

Table S7. Total energies E_{tot} and relative energies E_{rel} (in eV) as well as Mulliken spin densities on the Ni, S, and O atoms obtained from symmetry-unrestricted geometry optimizations on an approximate model of $[(\mathrm{PhTt}^{t\mathrm{Bu}})_2\mathrm{Ni}_2(\mu\text{-O})_2]$ **1** for various spin states as indicated. The indices l and r refer to the left and right half of the molecule, respectively.

	energy		spin density					
	E_{tot}	E_{rel}	Ni_l	Ni_r	O_l	O_r	S_l	S_r
$S = 1/2$, HS	–313.0599	+0.0505	+0.5548	+0.5548	+0.2092	+0.2092	+0.2166	+0.2166
$S = 1/2$, BS	–313.1104	0	+0.4759	–0.4758	+0.2435	–0.2440	+0.2114	–0.2109
$S = 3/2$, HS	–311.5558	+1.5546	+1.4464	+1.4464	+0.9195	+0.9195	+0.5712	+0.5712

Table S8. Energies (in eV) and compositions (in %) of the lowest unoccupied Ni1 d-based molecular orbitals obtained from a BS DFT calculation on an approximate model of $[(\mathrm{Tp}^{\mathrm{Me3}})_2\mathrm{Ni}_2(\mu\text{–O})_2]$ **4**. Only Ni 3d, O 2p, and N 2p orbital contributions are shown. Contributions from C and H atoms are negligible for these MOs.

		left		bis-μ-oxo			right	
level	energy	N	Ni1	p_x	p_y	p_z	Ni2	N
Ni1(xy),α	-2.790	6	41	28	3	0	7	0
Ni1(xy),β	-3.363	3	33	4	41	0	8	0
Ni1(xz),α	-3.667	7	56	0	0	17	2	0

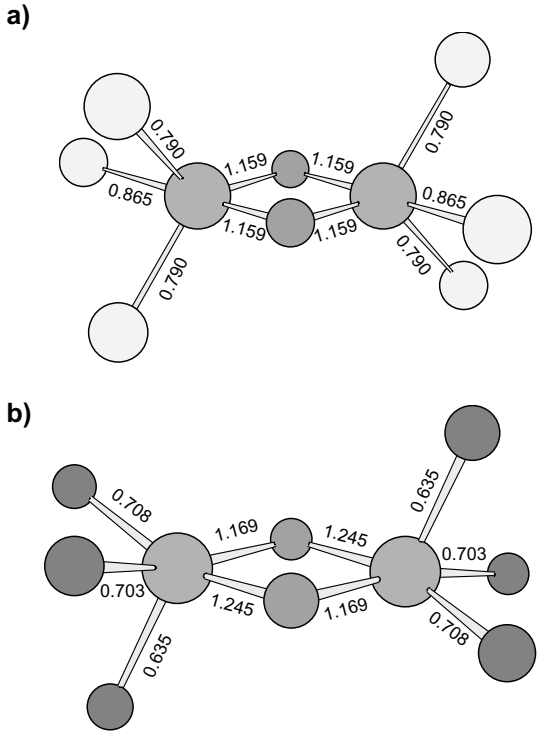

Figure S1. Comparison of the Ni–ligand bond orders in a) $[(\mathrm{PhTt}^{t\mathrm{Bu}})_2\mathrm{Ni}_2(\mu\text{-O})_2]$ **1** and b) $[(\mathrm{Tp}^{\mathrm{Me}_3})_2\mathrm{Ni}_2(\mu\text{–O})_2]$ **4**, as obtained from DFT computations in the respective BS ($\mathrm{M}_S = 0$) states.